

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 078 119**  
**A1**

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 82305354.1

(51) Int. Cl.<sup>3</sup>: **C 04 B 15/06**  
**C 01 B 33/24, B 01 J 3/04**

(22) Date of filing: 08.10.82

(30) Priority: 28.10.81 US 315695

(43) Date of publication of application:  
04.05.83 Bulletin 83/18

(84) Designated Contracting States:  
BE DE GB IT NL

(71) Applicant: Horton, William George  
Badgers Gill Batt House Road  
Stocksfield Northumberland(GB)

(72) Inventor: Horton, William George  
Badgers Gill Batt House Road  
Stocksfield Northumberland(GB)

(74) Representative: Middlemist, Ian Alastair  
W. Reid Sharpe & Co. 24 Portland Terrace  
Newcastle upon Tyne NE2 1QS(GB)

(54) Calcium silicate base materials.

(57) A calcium silicate based material is disclosed comprising a matrix of calcium silicate consisting predominantly of xonotlite and/or tobermorite to which silica, preferably finely divided silica such as silica fume, has been added to occupy the interstices of the matrix. Calcium ions, residual from the crystal forming reaction may be present or added as calcium oxide, calcium hydroxide or a calcium salt which dissociates in aqueous solutions excluding  $\text{CaCl}_2$  and other anions which may deleteriously affect the material. These then undergo a superficial reaction with the silica particles, providing a cementitious bond between the particles without significant loss of the thermal properties of the silica. The material has improved properties as regards to thermal insulation, shrinkage on drying, and compressibility, after heating at elevated temperatures.

EP 0 078 119 A1

ED250982

- 1 -

CALCIUM SILICATE BASED MATERIALS

This invention relates to improved calcium silicate materials and to processes for manufacture of such materials.

Calcium silicate materials comprising a crystalline  
5 matrix of calcium silicate consisting predominantly  
of xonotlite and/or tobermorite are known and used  
widely in applications involving hot face temperatures  
above about 600°C. These are produced generally by  
mixing silica with calcium hydroxide (usually as slaked  
10 lime) and autoclaving before or after moulding. United  
States Patent Specification No. 4238240 summarises a  
number of previous patents exemplifying such processes.  
The thermal insulating materials thus produced have  
limited life at above 1000°C and are generally, after  
15 heating fragile, and the materials may also be subject

ED250982

- 2 -

to a degree of superficial shrinkage on drying which creates production problems and defects in moulded articles, such as slabs, moulded from the materials.

It is also known to add a quantity of wood pulp  
5 or other cellulose fibres, rock wool, and/or  
diatomaceous earth. It has also been proposed, in  
British Patent Specification 1,462,242 to add clay or  
the like to a reacted slurry of hydrated calcium  
silicates, but this requires a longer moulding time  
10 and the shrinkage on drying of the moulded product  
increases proportionately to the amount of clay added.

An object of the invention is to provide a calcium  
silicate based material with improved thermal insulating  
properties and improved strength after heating, and  
15 reduced superficial shrinkage on drying.

The invention accordingly provides a calcium  
silicate based material comprising a crystalline matrix  
of calcium silicate consisting predominantly of xonotlite  
and/or tobermorite, characterised in that free silica  
20 has been added to the material to occupy interstices  
of the matrix.

LDO21082

- 3 -

Advantageously a source of calcium ions is also present, residual from the matrix-producing reaction, or added with or immediately after or before the addition of the free silica, such as for example  
5 a suspension of calcium oxide, or slaked lime.

The silica is preferably added in the form of a finely divided powder with a surface area in the range for example of  $10-250\text{m}^2/\text{gr}$ , such as silica fume recovered for example from the manufacture of silicon  
10 metal or from the manufacture of ferro silicon.

The invention also provides a method of making a calcium silicate based material comprising reacting silica and calcium oxide to produce a matrix of crystalline calcium silicate consisting predominantly  
15 of xonotlite and/or tobermorite, characterised in that after completion of the reaction, free silica is added thereto to occupy interstices of the matrix.

Advantageously calcium ions are also present or added, in for example the form of a solution of calcium  
20 oxide or slaked lime preferably in a quantity sufficient to react with surface layers only of the silica particles

LDO21082

- 4 -

whereby the particles may be "cementitiously" bonded together, without substantial loss of the thermal properties of the silica.

5 The slurry of calcium oxide and silica used to produce the crystalline matrix may additionally contain a small quantity of manganese, magnesium or other ions capable of being incorporated in the calcium silicate crystal structure. Such additions enable a higher solids content to be present in the  
10 slurry without the expected increase in viscosity. They do however unacceptably increase the thermal shrinkage at  $1000^{\circ}\text{C}$  which is more than offset by the addition of free silica.

The slurry of lime and silica is preferably auto-  
15 claved, after which silica (and calcium ions or a suitable source of such ions as required) are added at a temperature necessary to permit the cementitious reaction to occur (usually above  $75^{\circ}\text{C}$ ) together with a suitable quantity and type of non-asbestos fibre.  
20 The slurry is then moulded. The resulting slabs are then dried, or may be subjected to further autoclaving before drying.

ED250982

- 5 -

Suitable calcium salts which dissociate in aqueous solutions may be used as a calcium ion source, provided the anion of the salt does not itself have adverse effects on the product. For this reason  
5 calcium chloride is not suitable.

The material and method of the invention will now be further described and the inventive concept explained hereinafter and with reference to the following examples.

Example I

10      Experiment illustrating the underlying concept  
of the Invention

10gr. of silica fume (a very finely divided form of silica having a surface area of  $14\text{m}^2/\text{gm}$ ) was stirred with 1 litre of distilled water at  $80^\circ\text{C}$ . The slurry  
15 was filtered and the resultant filter cake completely dried in a laboratory oven at  $110^\circ\text{C}$ . The dried cake crumbled easily between the fingers.

The above steps were repeated using the hot filtrate from a well reacted slurry originally comprising 20 equimolar proportions of calcium oxide and silica in

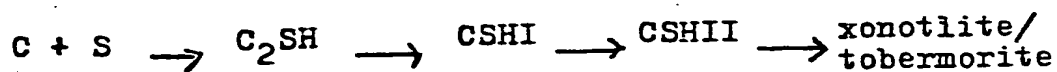
ED250982

- 6 -

distilled water and having a pH of 9-9.5. This dried cake was significantly less crumbly.

These observations may be explained in that Jennite or other well recognised species of calcium silicate are formed under these conditions. Due to the limited quantity of calcium ions present in the latter filtrate, the reaction is probably superficial only, but sufficient to provide adequate cementitious bonding between the particles of silica, and possibly also to the existing calcium silicate if, as proposed in the present invention, this reaction were carried out after formation of a crystalline matrix of calcium silicate.

The reaction between lime and silica to make calcium silicate proceeds in several stages and is well-known. It is generally agreed that this reaction can be represented as:-



where C = CaO, S = SiO<sub>2</sub>, and H = H<sub>2</sub>O.

ED250982

- 7 -

The reaction is time and temperature dependant.  
A description of this multi-step process is given in Canadian Patent 601,124 at column 3 line 41 to column 4 line 11.

5        In one embodiment of this invention, to make high temperature resistant calcium silicate with good thermal shrinkage and a high compressive strength after heating, free silica is added at a stage where substantially only xonotlite is present, i.e. there  
10 is no free lime or free silica left from the reaction constituents but sufficient calcium was present to participate in a surface reaction with the added silica in the manner described. In another embodiment the reaction product also includes some tobermorite.

15        In a developed embodiment, the free silica is added with a source of calcium ions, by way of non-exclusive example slaked lime to promote a superficial reaction of the kind bonding the silica particles as explained in connection with Example 1 above.

20        Free silica can be added at that stage of the reaction between lime and silica slurry whereby the



ED250982

- 8 -

thermal properties, and therefore physical properties of the free silica are not significantly modified as a result of reaction with excess calcium ions arising from incomplete reaction between the lime and silica initially present in the slurry. This is probably at the CSHI stage or later.

By adding free silica a significant improvement in the thermal shrinkage of the dried moulded material made from a well reacted slurry on drying, is achieved. Consistently the thermal shrinkage at  $1000^{\circ}\text{C}$  for 24 hours is about 0.6% to 0.9%, about 1.2% at  $1040^{\circ}\text{C}$  and about 3.0% at  $1065^{\circ}\text{C}$  when free silica is added to the calcium silicate matrix. Promotion of a bonding reaction by adding calcium ions to produce a superficial reaction does not significantly affect the advantage gained in this respect in adding the free silica.

Further examples of the effects of adding free silica in accordance with this invention can be seen from the following examples.

Example 2

ED250982

- 9 -

Without free silica

The reaction product was prepared by reacting approximately equimolar amounts of lime and silica for 45 minutes at 150°C, and then for 3 hours above 5 170°C. Five percent by weight of wood pulp and mineral wool in equal amounts was added to the slurry produced by the reaction. No manganese acetate was added to the reaction constituents. The reaction product was moulded and then calcined for 24 hours at 10 1000°C. Thermal shrinkage without any addition of free silica of three separately reacted and prepared samples was 1.16%; 2.98%; and 2.87% respectively.

Example 3With free silica

15 The reaction product was prepared in the same manner as in Example 2, but manganese acetate was added to the reaction constituents. The manganese acetate addition was at the level of 1.5%. Five percent wood pulp was added, instead of 2.5% each of 20 wood pulp and mineral wool, and 10% by weight of free silica was added to half the reaction product

ED250982

- 10 -

and the resultant liquor moulded. The remaining half of the liquor was moulded without any silica addition. The slabs were dried and calcined at 1000°C. The variation in the fibre addition is not believed to have  
 5 affected the result. The comparative results obtained are set out below in Table 1.

TABLE 1

<u>Reaction</u>		<u>Without 10% free silica</u>	<u>With 10% free silica</u>
		(Example 2)	(Example 3)
10	1	5.54'	0.86
	2	4.08	0.80
	3	5.98	0.87
	4	5.99	-
15	5	-	0.81
	6	-	0.73
	7	-	0.63
	8	-	0.73

It will thus be seen that the addition of free  
 20 silica not only materially reduces the shrinkage of the material (from about 2% to under 1%) but also obviates the excessive thermal shrinkage caused by addition of "doping" ions such as manganese.

ED250982

- 11 -

Example 4Added silica with calcium ions

3.4 litres of well reacted calcium oxide and silica made by reacting equimolar proportions in aqueous suspension and recognised as well reacted by  
5 X-ray diffraction, were divided into 2 portions. To the first portion (1.7 litres) 100ml. of an aqueous slurry of slaked lime with 5 gr. well dispersed wood pulp and 10g. of silica fume were added. The resultant aqueous mix was heated to 90°C and filtered in a  
10 large Buchner funnel. The resultant disc like cake was dried at 110°C to constant weight.

This procedure was repeated with the second half of the liquor, but without addition of the 10 gr. of silica fume. The diameters of the wet and dried cakes  
15 were measured and the superficial drying shrinkages measured.

The results showed that superficial shrinkage without silica addition averaged 10% but with the silica shrinkage averaged 4% approx.

ED250982

- 12 -

Note The superficial shrinkage for a given reaction liquor is dependant upon many factors and in practice can vary usually over the range 3-12%. In all cases the additions of free silica reduces the superficial shrinkage. The addition of calcium ions by way of slaked lime does not significantly effect this property achieved by the silica addition, but does improve the strength of the material.

The accompanying drawing is a plot of heat transmission ( $\lambda$ ) against material density in  $\text{Kg/m}^3$  for a calcium silicate material without silica addition (full line curves) and with silica addition (broken line curves), at different temperatures.

Curves A and B are derived from measurements taken at  $550^\circ\text{C}$  mean temperature. Curves C and D are derived from measurements taken at  $500^\circ\text{C}$  mean temperature. Curves E and F are derived from measurements taken at  $450^\circ\text{C}$  mean temperature. Curves G and H are derived from measurements taken at  $400^\circ\text{C}$  mean temperature.

The broken line curves show that the thermal conductivity of the material according to this invention is significantly lower at any given temperature than

LDO21082

- 13 -

that of calcium silicate made without free silica.  
The addition of free silica of a much higher surface area will greatly enhance this difference.

The measurements of the free silica containing material  
5 have only been conducted up to densities of about  
150Kg/m<sup>3</sup>, but the curves may reasonably be extrapolated  
to have the same general shape and gradients as those  
for the material without free silica which have been  
measured up to densities of about 200Kg/m<sup>3</sup>.

10 The material according to the invention has the  
additional advantage that whereas most calcium  
silicate materials tend to soften after calcination,  
when free silica with or without calcium ion aided  
cementitious binding of the silica are added, the  
15 compressive strength of the calcium silicate is  
effectively unchanged as illustrated by the following  
data:-

T A B L E 2

Compressive strength (KiloNewtons per square metre)	
Before treating to 1000°C for 24 hours	- 1350KN/m <sup>3</sup>
20 After heating to 1000°C for 25 hours	- 1625KN/m <sup>3</sup>

ED250982

- 14 -

CLAIMS

1. A calcium silicate based material comprising a crystalline matrix of calcium silicate consisting predominantly of xonotlite and/or tobermorite, characterised in that free silica has been added to  
5 the material to occupy interstices of the matrix.
2. A material according to claim 1 characterised in that a source of calcium ions is present or has been added to the matrix.
3. A material according to claim 2 characterised  
10 in that the source of calcium ions is any one of calcium oxide; calcium hydroxide; or a calcium salt which dissociates in aqueous solution and the anion of which has no disadvantageous effect on the properties of the material.
- 15 4. A material according to claim 1, 2 or 3 characterised in that the free silica has a high surface area per unit mass greater than  $5\text{m}^2/\text{gr.}$  and is amorphous in structure with generally spherical particles.

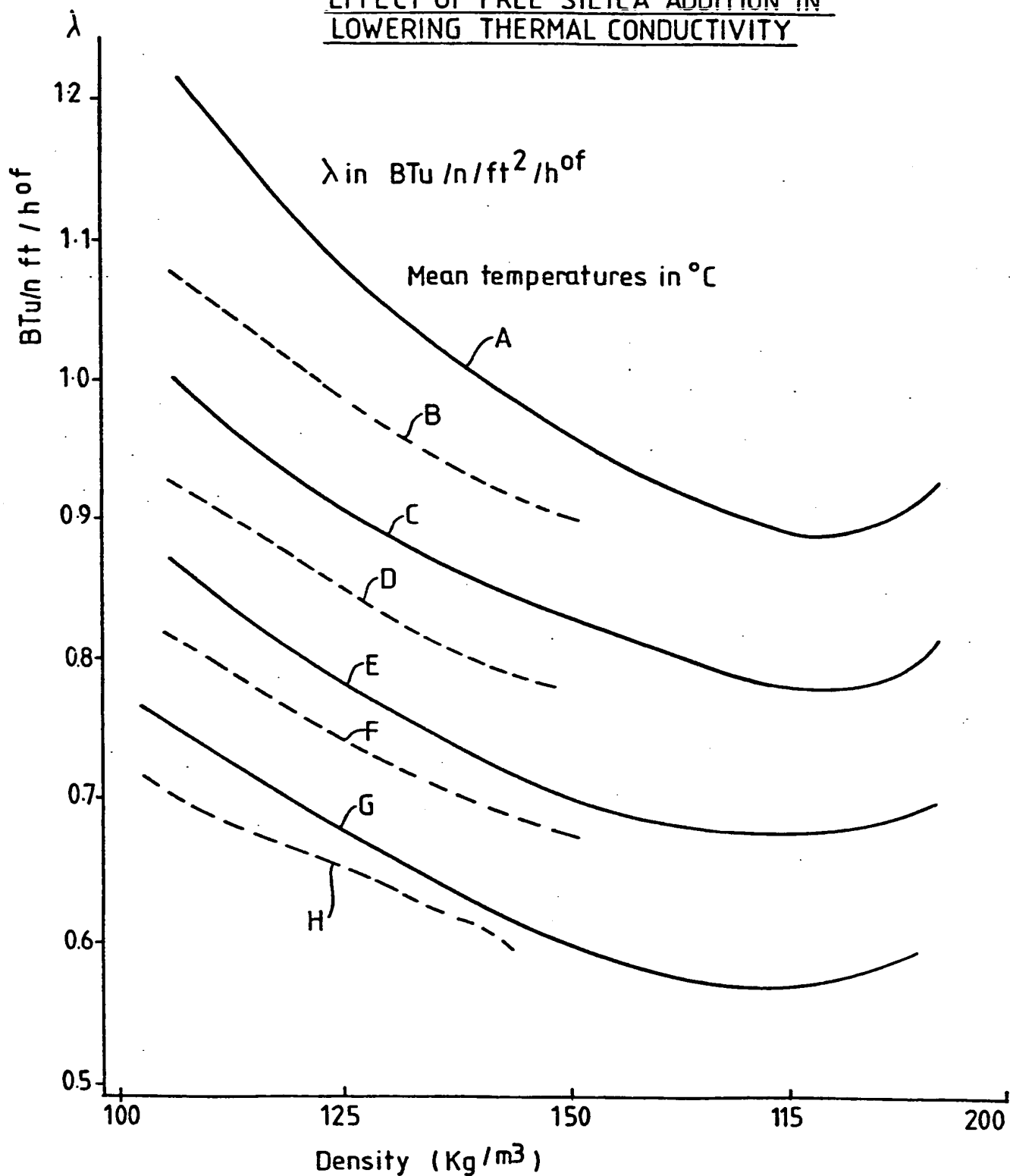
ED250982

- 15 -

5. A material according to claim 4 characterised in that the surface area of said free silica is in the range of 10 to 250 m<sup>2</sup>/gm.
6. A material according to claim 4 or 5 characterised in that said free silica is silica fume recovered from the manufacture of silicon metal or from the manufacture of ferro silicon.
7. A method of making a calcium silicate based material comprising reacting silica and calcium oxide to produce a matrix of crystalline calcium silicate consisting predominantly of xonotlite and/or tobermorite, characterised in that after completion of the reaction, free silica is added thereto to occupy interstices of the matrix.
8. A method according to claim 7 characterised in that calcium ions are present in solution from the reaction forming the matrix.
9. A method according to claim 7 characterised in that a source of calcium ions is added to the material.



EFFECT OF FREE SILICA ADDITION IN  
LOWERING THERMAL CONDUCTIVITY





European Patent  
Office

# EUROPEAN SEARCH REPORT

0078119

Application number

EP 82 30 5354

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	--- EP-A-0 007 585 (MINORA, FORSCHUNGS- UND ENTWICKLUNGSGESELLSCHAFT FÜR ORGANISCHE UND ANORGANISCHE BAUSTOFFE) * Claims 1,2,4 *	1,6	C 04 B 15/06 C 01 B 33/24 B 01 J 3/04
A	--- DE-A-2 936 169 (K.K. OSAKA PACKING SEIZOSHO) * Page 30, last 4 lines - page 31, paragraph 1; claims 1,21 *	1	
A	--- EP-A-0 009 836 (WARRIOR INSULATION COMPANY B.V.) * Claims 1-40 *	1	
A	--- GB-A-2 000 753 (JOHNS MANVILLE CORP.) * Claims 1-4 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)  C 04 B C 01 B B 01 J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02-02-1983	Examiner STANGE R.L.H
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO Form 1603 03 82